N O T I C E

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SPECTROLAB

"HIGH RESOLUTION, LOW COST SOLAR CELL CONTACT DEVELOPMENT"

FINAL REPORT
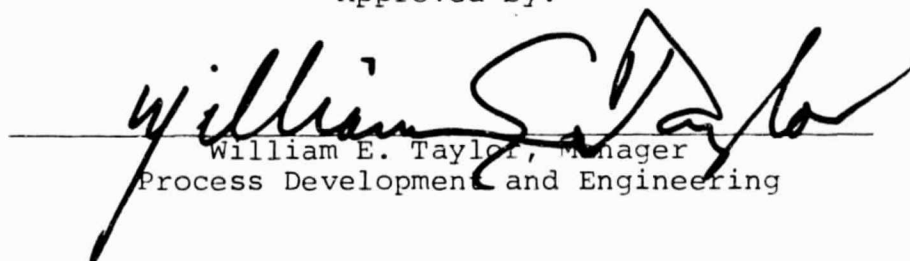
December 1979

Contract 955298

Prepared for:

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TABLE OF CONTENTS

1.0 SUMMARY STATEMENT

Experimental work demonstrating the feasibility of the MIDFILM process as a low-cost means of applying solar cell collector metallization was completed during this contract. Cell efficiencies of above 14% (AM1, 28°C) were achieved with fritted silver metallization. Environmental tests suggest that the metallization is slightly humidity sensitive and degradation is observed on cells with high series resistance. The major yield loss in the fabrication of cells was due to discontinuous grid lines, resulting in high series resistance. Standard lead-tin solder plated interconnections do not appear compatible with the MIDFILM contact.

Copper, nickel and molybdenum base powder were investigated as low-cost metallization systems. The copper based powder degraded the cell response. The nickel and molybdenum base powders oxidized when sintered in the oxidizing atmosphere necessary to ash the photoresin.

2.0 INTRODUCTION

This Final Technical Progress Report covers the six month period ending December 31,1979. The scope of the contract covers the demonstration of feasibility of forming solar cell collector grid contacts by the MIDFILM® process. This is a proprietary process developed by Ferro Corporation, a subcontractor for the program. The cost effectiveness of the MIDFILM process for the collector grid contacts was found to be better than that of screen printing processes.

The MIDFILM process attains a line resolution comparable to photoresist methods with a process related to screen printing. The surface to be processed is first coated with a thin layer of photopolymer material. Upon exposure to ultraviolet light through a suitable mask, the polymer in the non-pattern area cross-links and becomes hard. The unexposed pattern areas remain tacky. The conductor material is applied in the form of a dry mixture of metal and frit particles which adhere to the tacky pattern area. The assemblage is then fired to ash the photopolymer and sinter the fritted conductor powder.

This effort was divided into four tasks. Task I was to explore and identify two or more conductive powder compositions and corresponding process parameters which, used as collector metallization, produce solar cells which show useful electrical and mechanical properties. Task II was to conduct environmental evaluations on solar cells made with two different powder compositions applied as collector metallization by the MIDFILM process. The environmental evaluation including exposure to humidity, thermal cycle, boiling water and lead wire soldering. Task III was to conduct an exploratory investigation of the use of nickel or other base metal applied as collector metallization by the MIDFILM process. Task IV was to compile the necessary information, in the form of SAMICS Format A, to enable an economic evaluation of the process in comparision with other processes for applying collector contact metallization.

3.0 TECHNICAL DISCUSSION

3.1   EXPLORATORY DEVELOPMENT

Five conductive powder compositions were selected as possible
MIDFILM metallization candidates. They were (compositions in
weight per cent):

1. 98% Fine flake silver powder; 2% Drakenfeld frit
   Metz "C" (80)Pb),(10)B_2O_3,(10) SiO_2.
2. 98% Ferro silver powder; 2% Drakenfeld frit.
3. TFS 3347 composition without screening medium.
4. 98% Ferro silver powder; 2% Spectrolab frit #2-.
5. 98% Ferro silver powder; 2% Ferro Bismuth frit #3.

The first four compositions were selected on the basis of ex-
perience at Spectrolab with screen printing paste. The fifth
was selected on recommendations from Ferro. A standard 2 cm x
4 cm aerospace front metallization pattern was choosen, Figure 1.

Partial processed wafers were prepared at Spectrolab by the fol-
lowing process sequence:

1. Etch wafers in 30% NaOH.
2. Rinse.
3. Diffuse to 25-70 ohms/□ sheet resistance with PX-10
   polymeric spin-on diffusion source.
4. Print and fire aluminum back.
5. Strip diffusion oxide and clean aluminum back.
6. Laser scribe and cleave.

Figure 1

GRID PATTERN TAKE FROM 901708-1

Kodak type glass (UV Transmissive)
Gridlines width = 0.0012 inches

2.75±.25

1.584

48 Grid Lines
Equally Spaced
@ .033±.001
(C̵ to C̵) =
1.551±.001
(Tol.Non-Accum)
(Typ.2 places)

←.031 →

←.745±.002 →

2.75± .25

POSITIVE GLASS MASTER
(6318-1)
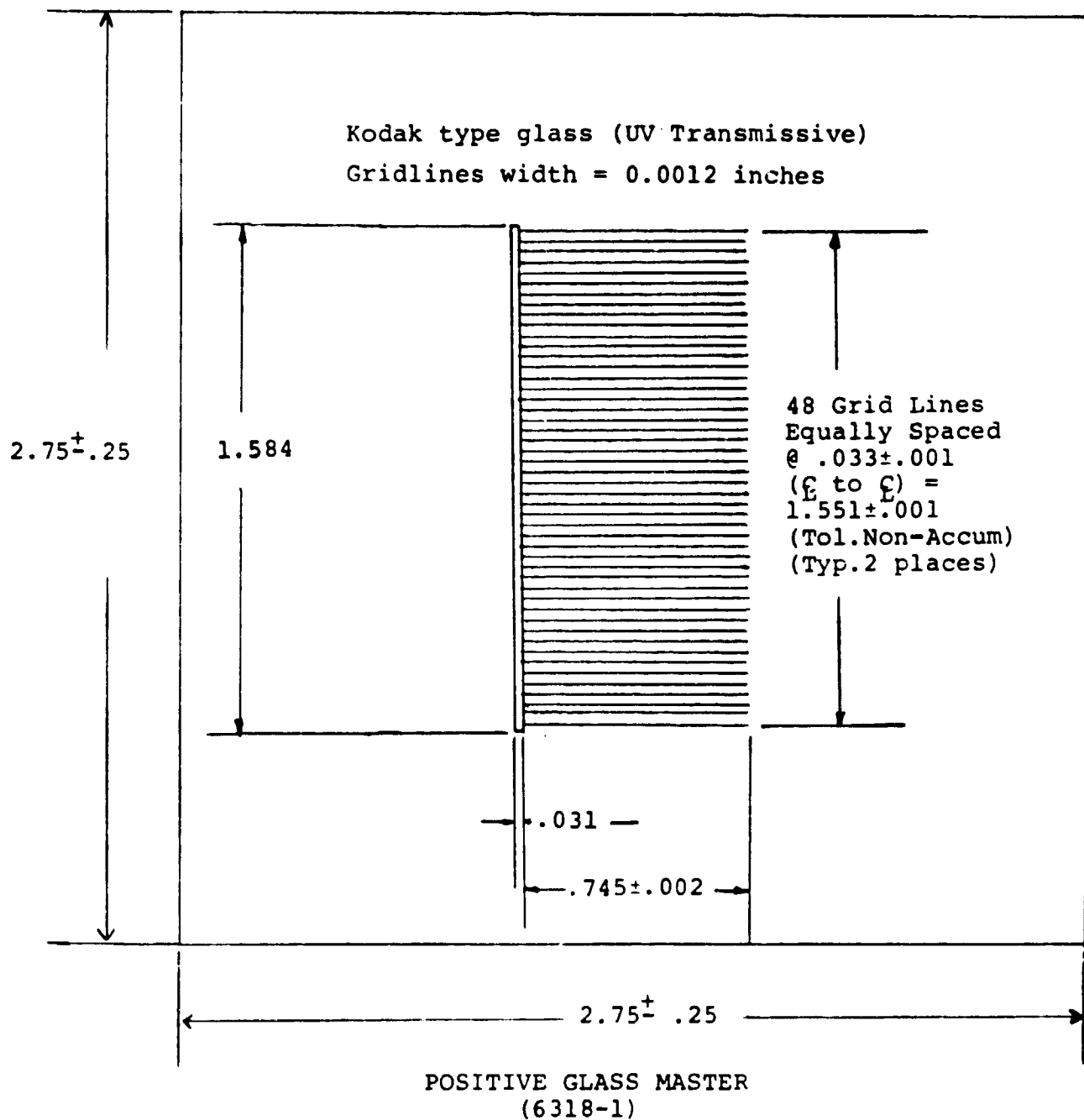
These wafers were sent to Ferro corporation for the application of the MIDFILM contact.

Ferro Corporation cleaned the wafers in accordance with the procedure described in Appendix 1 and applied the MIDFILM contact in accordance with the procedure described in Appendix 2. These metallized wafers where then shipped back to Spectrolab for the firing step.

Control cells were fabricated by screen printing silver paste onto the same lot of wafers that were sent to Ferro Corporation. Table 1 list the cell characteristics of the control cells. The five lots of wafers received from Ferro Corp., were fired at a variety of times and temperatures in order to determine the optimum firing conditions and evaluate the conductive powders. Table 2, 3, 4, 5 and 6 list the cell characteristics of composition 1, 2, 3, 4 and 5 respectively. Powder composition 4 either had low short circuit current (I_{sc}) or low open circuit voltage (V_{oc}) or both in all cases. The other compositions had a high I_{sc} and V_{oc} in some cases but did not have a good curve shape (poor curve fill factor). Further analysis of these cells revealed serious problems with series resistance, Table 7.

Tally Surf measurements of the gridlines were performed and the series resistance of the grid pattern was calculated for each composition, Table 7 (see Appendix 3 for calculations of series resistance). These calculations revealed a series resistance difference between the powders associated with differences in gridlines thickness. The flake powder gridlines were 4 to 5 μ thick, while the "spherical" powder gridlines were 7 to 8.5 μ thick. The gridlines were examined under a microscope. Typical structures are shown in Figure 2 through 5. Broken gridlines (area A) and voids (area B) were found on cells with poor output at load (Figures 2 and 3). Continuous gridlines with few voids (areas A and B) were found on cells with high outputs (Figures 4 and 5).

TABLE 1

Screen Printed Control Cells

(TFS 3347 + 2% n-Diffusol) (No AR Coating)

Cell No.	Sheet ($\Omega/\square$)	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{shunt} (Ω)	R_{series} (mΩ)
10	27.9	610	195	178	69	155
50	29.5	609	200	180	53	125
88	28.0	606	199	173	37	115
101	52.1	608	205	188	83	160
148	53.9	604	199	162	15	-
189	46.1	605	200	166	35	260
201	?5.4	610	190	176	98	-
250	25.0	610	190	171	104	255
294	24.1	602	179	165	156	200
300	25.4	612	194	183	91	75
349	30.1	609	201	181	51	150
394	28.5	607	195	177	72	-
* 151	50.2	609	206	189	93	175
255	26.6	610	193	179	104	135
* 353	30.3	607	200	161	119	-

* Not edge etch prior to front metallization

TABLE 2

LOT #1   (NO AR COATING)

Temp (°C) \ Time (Sec)	10	20	30	40	50	60	75	80	90	100
V_{oc} (mV)										
650	553 (1)	598 (1)	587 (1)	591 (1)	596 (1)	597 (6)	601 (3)	599 (2)	597 (2)	594.5 (2)
700	567 (1)	588 (1)	601.3 (4)	599.5 (4)	597.3 (3)	579 (1)	---	---	---	---
750	592 (1)	593 (1)	602 (1)	597 (1)	594 (1)	590 (1)	---	---	---	---
I_{sc} (mA)										
650	73	213	206	199	206	188.8	206.7	193	186.5	189.5
700	70	185	196	183.3	190.7	171				
750	185	174	178	173	161	157				
I_{500} (mA)										
650	13	29	37	54	79	87	114.7	110	77	86
700	22	43	129.3	100.8	96.7	79				
750	65	137	128	137	110	82				
R_{sh} (Ω)										
650	5000	556	143	91	152	108.5	52.2	51.5	74.8	59
700	1250	135	40.8	47.9	50.7	29				
750	70	27	22	51	24	25				

AVERAGE
(SAMPLE
SIZE)

TABLE 3

LOT # 2 (NO AR COATING)

(°C) Temp \ Time (Sec)	10	20	30	40	50	60	70	75	80		100	
					V_{oc} (mV)							
650	532 (1)	572 (1)	580 (1)	597 (1)	597 (1)	599.4 (5)	---	599.7 (3)	588.5 (2)	598 (2)	595 (2)	
700	572 (1)	599 (1)	594 (1)	593 (1)	599.7 (3)	600.3 (4)	600 (2)					
750	582 (1)	585 (1)	590 (1)	590 (1)	577 (1)	591 (1)						
					I_{sc} (mA)							
650	38	94	158	170	192	192.8	---	173.3	174	186.5	179	
700	68	182	185	178	190	183	187.5					
750	153	169	172	159	146	171						
					I_{500} (mA)							
650	7	23	30	62	66	109.2	---	121.3	81	77	122.5	
700	14	82	74	99	111.3	138.5	134.5					
750	40	74	71	84	72	115						
					R_{sh} (Ω)							
650	5000	5000	66	42	85	50.6	---	34.4	28.5	40.7	30	
700	833	39	26	18	24.4	27	22.8					
750	42	23	27	21	12	23						

TABLE 4

LOT #3   (NO AR COATING)

(°C) Temp \ Time (Sec)	10	20	30	40	50	60	80	100	120
	V_{OC} (mV)								
650	567 (1)	587 (1)	596 (1)	601 (1)	580 (1)	594.7 (3)	593 (4)	600.2 (5)	591 (2)
700	591 (1)	503 (1)	597.7 (3)	602.3 (3)	596 (3)	601 (1)			
750	599 (1)	559 (1)	605 (1)	592 (1)	594 (1)	592 (1)			
	I_{sc} (mA)								
650	187	190	166	208	108	195.7	191.5	198.2	187.5
700	221	206	204	202	187.3	201			
750	183	197	195	197	184	182			
	I_{500} (mA)								
650	45	38	58	111	30	91.3	90.8	123.4	57.5
700	51	89	96.7	118.7	93.7	96			
750	65	75	167	93	98	71			
	R_{sh} (Ω)								
650	5000	1000	357	333	385	75.3	109	96.5	73.5
700	5000	217	91.2	57.9	81	102			
750	833	50	89	49	32	48			

TABLE 5

LOT #4   (NO AR COATING)

(°C) Temp	Time °C	10	20	30	40	50	60	80	100	
					V_{oc} (mV)					
	650	578 (1)	588 (1)	547 (1)	523 (1)	534 (1)	564.6 (5)	516.4 (5)	524.3 (3)	
	700	586 (1)	478 (1)	536.3 (4)	524.8 (4)	488 (3)	471 (1)			
	750	597 (1)	537 (2)	487 (1)	426 (1)	505 (1)	404 (1)			
					I_{sc} (mA)					
	650	98	111	124	118	144	209.4	163.4	180.7	
	700	104	110	197.8	163	133.3	149			
	750	201	198	173	134	193	139			
					I_{500} (mA)					
	650	15	26	19	12	20	67.8	33.8	23.7	
	700	16	Ø	36	40.3	4.7	Ø			
	750	60	40	Ø	Ø	9	Ø			
					R_{sh} (Ω)					
	650	25000	455	135	139	139	74.4	70.9	43.1	
	700	2500	68	30.4	70.5	44.1	36			
	750	200	27	19	31	20	20			

TABLE 6

LOT # 5 (NO AR COATING)

Temp (°C) / Time (°C)	10	20	30	40	50	60	80	100	
V_{oc} (mV)									
650	551 (1)	589 (1)	589 (1)	600 (1)	594 (1)	593.7 (6)	596.3 (5)	597 (4)	
700	543 (1)	591 (1)	597 (4)	595.8 (4)	591 (3)	595 (1)			
750	584 (1)	498 (1)	454 (1)	581 (1)	567 (1)	560 (1)			
I_{sc} (mA)									
650	62	118	117	179	138	169.8	179	126.8	
700	47	110	155.8	180.3	182	168			
750	111	146	120	179	142	147			
I_{500} (mA)									
650	17	23	35	46	43	59.5	58.6	73.5	
700	10	24	56.5	102.5	76.3	62			
750	24	9	∅	53	33	32			
R_{sh} (Ω)									
650	2500	1667	250	193	227	57.2	22.	38.6	
700	1000	278	63.5	33.8	22.2	34			
750	294	18	9.5	17	20	13			

TABLE 7

Resistance of Cell

LOT		1	2	3	4	5
Total resistance (mΩ)	1)	450	290	620	−	450
	2)	375	100	325	−	925
	3)	1050	1275	1050	−	1860
	4)	575	216	525	−	
Computed resistance: Gridline Thickness		4μ	8.5μ	5μ	7μ	8.5μ
Base Resistance (mΩ)		3.92	3.92	3.92	3.92	3.92
Diffuse Layer Resistance (mΩ)		3.90	3.90	3.90	3.90	3.90
Gridline Resistance (mΩ)		51.0	24.0	40.8	29.2	24.0
Ohmic Collector Resistance (mΩ)		14.3	6.72	11.5	8.2	6.72
Total (cal.) Resistance (mΩ)		50.0	28.3	41.4	31.4	28.3
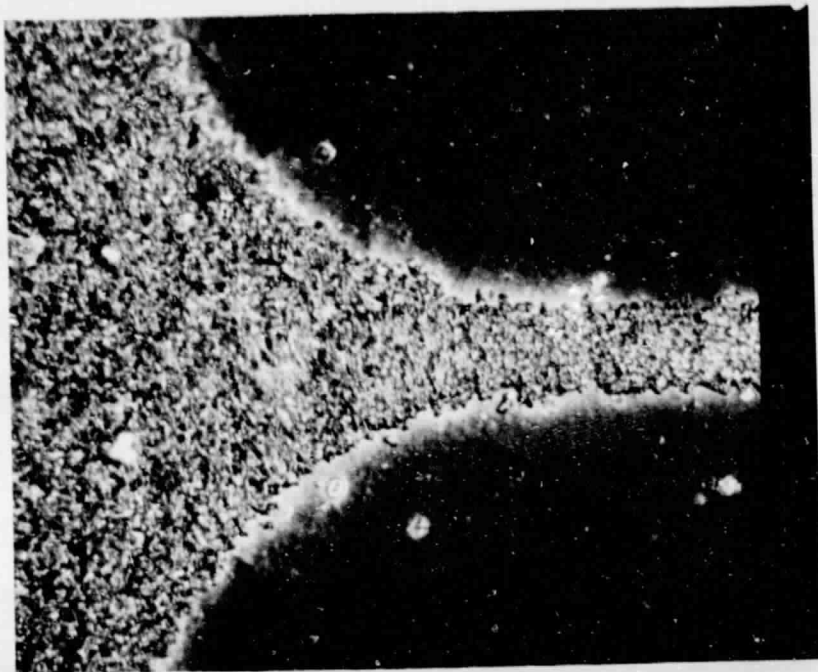
FIGURE 2

Good Metallization of Composition No. 2. 250X Mag.

Cell #	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (Ω)
227	604	198	168	39.1
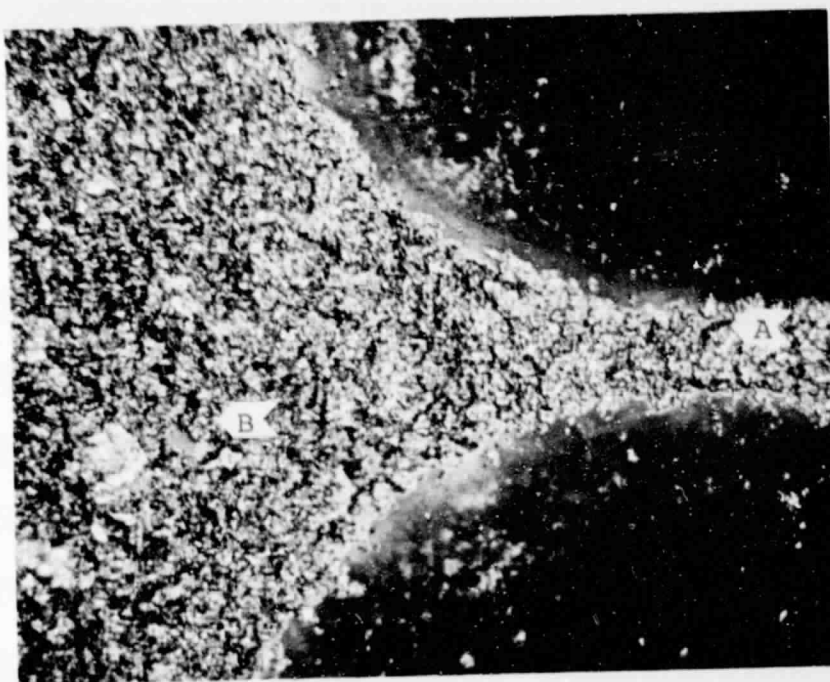
FIGURE 3

Good Metallization of Composition No. 3. 250X Mag.

Cell #	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (Ω)
319	604	206	177	131.6
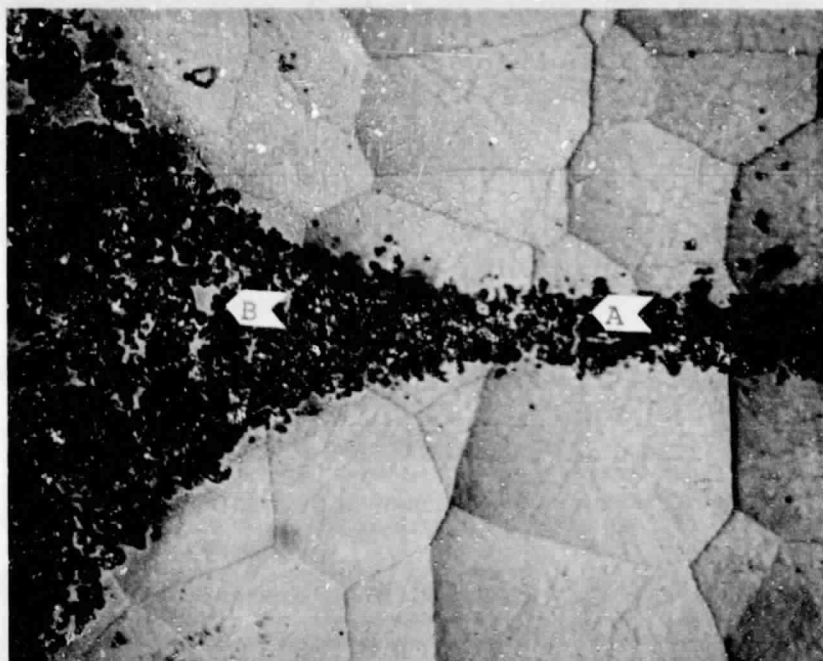
FIGURE 4

Poor Metallization of Composition No. 3. 250X Mag.

Cell #	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (Ω)
369	600	188	80	70.4
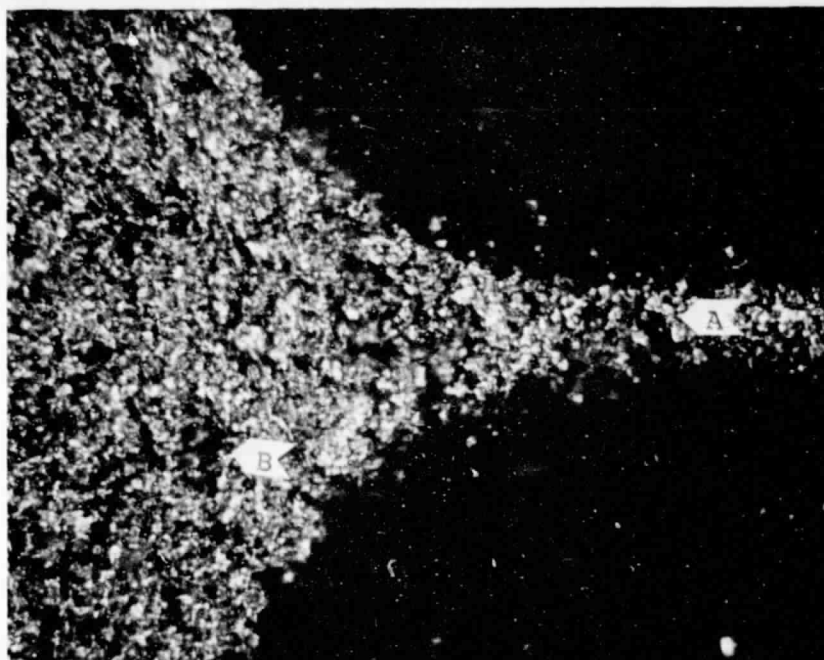
FIGURE 5

Average Metallization of Composition No. 5. 250X Mag.

Cell #	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (Ω)
19	593	167	66	48.5

-14-

In order to gain a better understanding of the powder-silicon
interaction, Scanning Electron Microscopy (SEM) was
performed on cells fabricated from compositions 2 and 3. The
structure of the respective silver gridlines are shown in Figures
6 and 7. The gridlines fabricated from composition 2 were dense
with good continuity whereas the gridline fabricated from compo-
sition 3 was incomplete and possible discontinuous. The silver
was then removed with nitric acid to expose the glass frit-
silicon interface. The frit-silicon contact area of composition 2,
shown in Figure 8, is limited and may result in a contact resistance
problem. The wetting characteristic (frit-silicon contact) of the
frit in composition 3 was good (Figure 9) and should not present
any contact resistance problem as long as the frit thickness is
held at a minimum. Further SEM analysis of the cross-section
of a Composition 2 gridline showed voids under the gridline,
indicating additional possibility for a contact resistance problem,
Figure 10. The wetting characteristics of composition 3 appear
to be good in the cross-section view, Figure 11.

The results of the Exploratory Development Task indicated that
two of the powder metal compositions have promising potential.
Figure 12 and 13 show output curves for the best cells fabricated
from composition 2 and 3 respectively. Composition 2 has the
virtue of "spherical" type powder which results in a thick, con-
tinuous gridline and lower series resistance. The frit in com-
position 2 has poor wetting characteristic which may contribute to
series resistance. Composition 3 has the virtue of having the
best shunt resistance, and good wetting characteristics. Both
of these virtues are probably associated with the frit in composi-
tion 3 and not the flake silver in this composition.

Figure 6

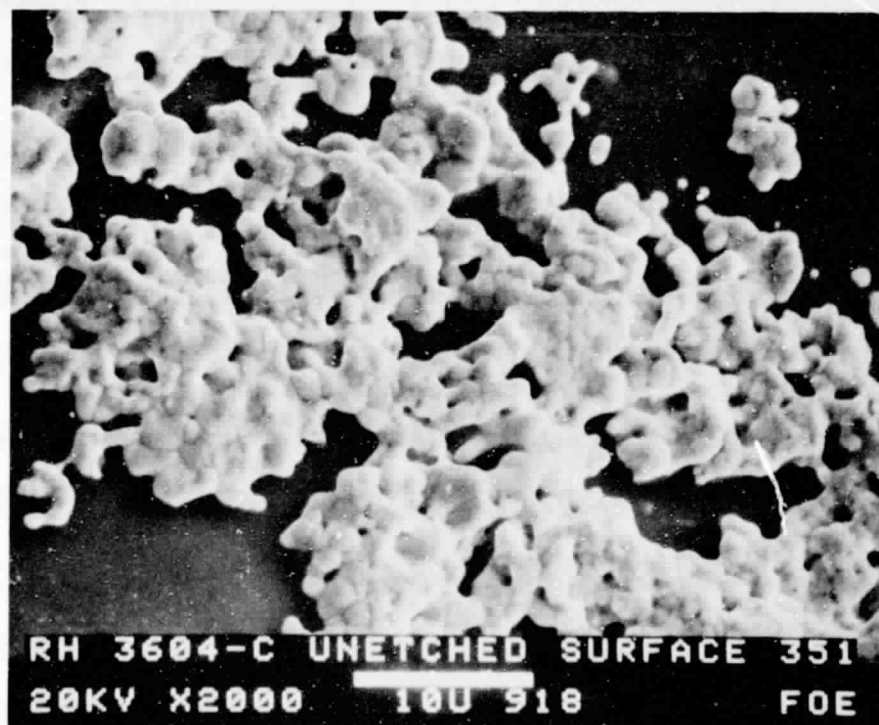## SURFACE OF THE APPLIED AND FIRED SILVER-FRIT POWDERS

RH-3604-B UNETHCED SURFACE 273
20KV X2000 10U 914 FOE
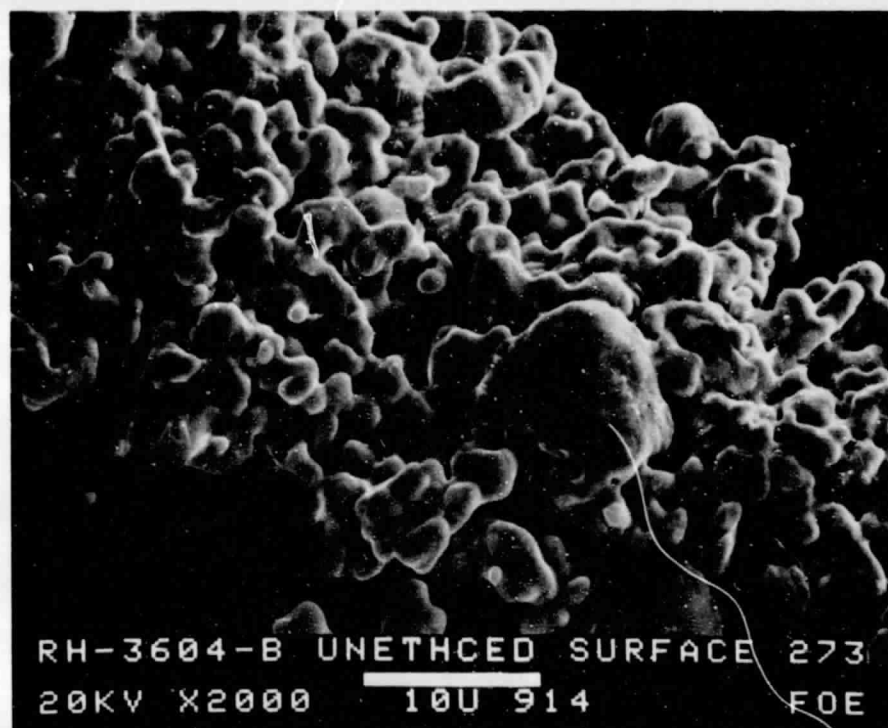
Composition 2, 2000X Magnification

Figure 7

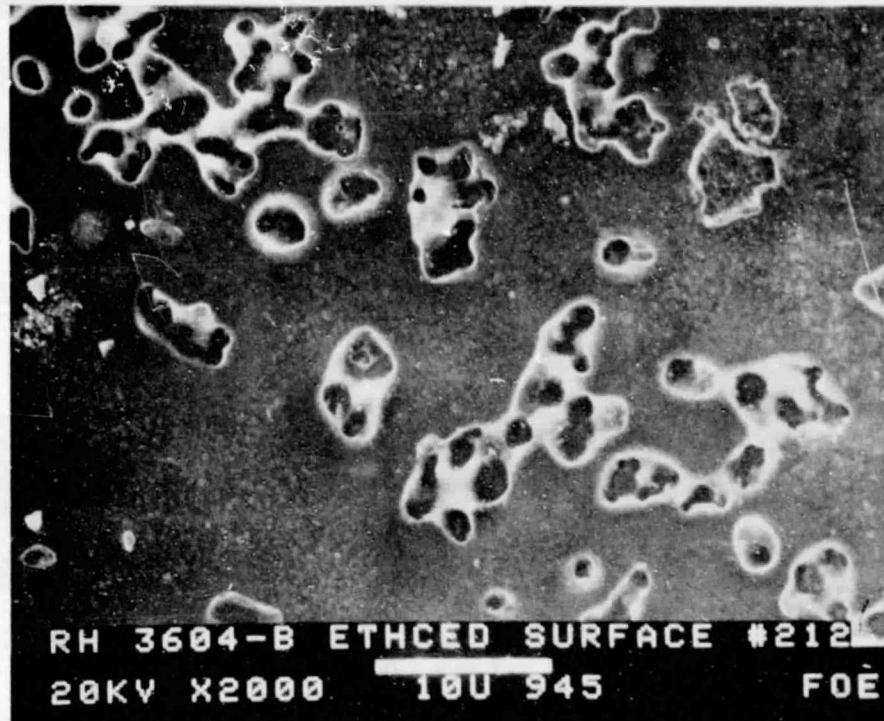RH 3604-C UNETCHED SURFACE 351
20KV X2000 10U 918 FOE

Composition 3, 2000X Magnification
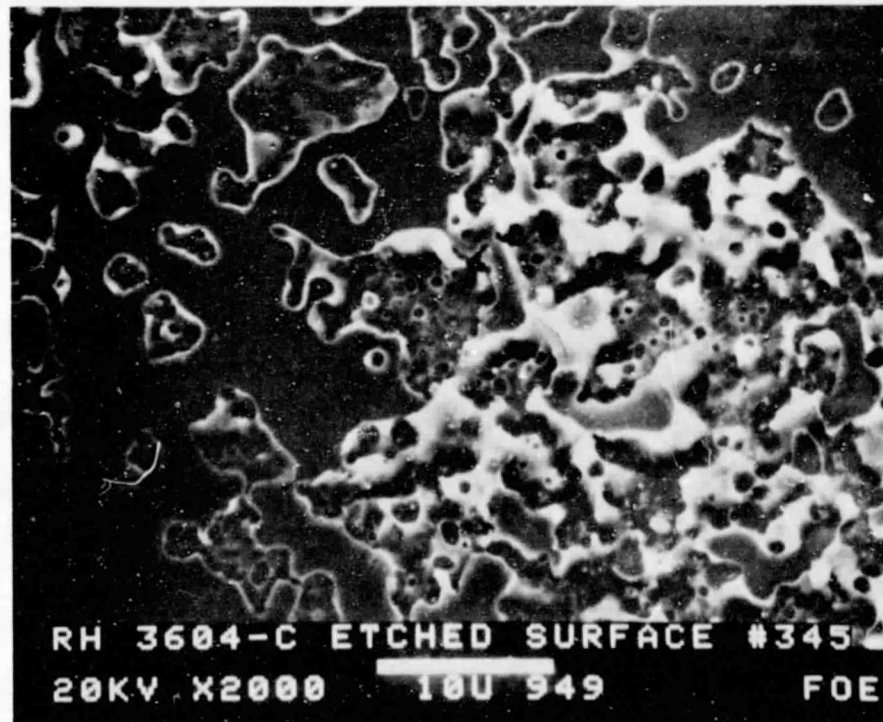
-16-

Figure 8

SURFACE OF THE SILICON CELL AFTER SILVER
WAS ETCHED AWAY LEAVING ONLY THE FRIT

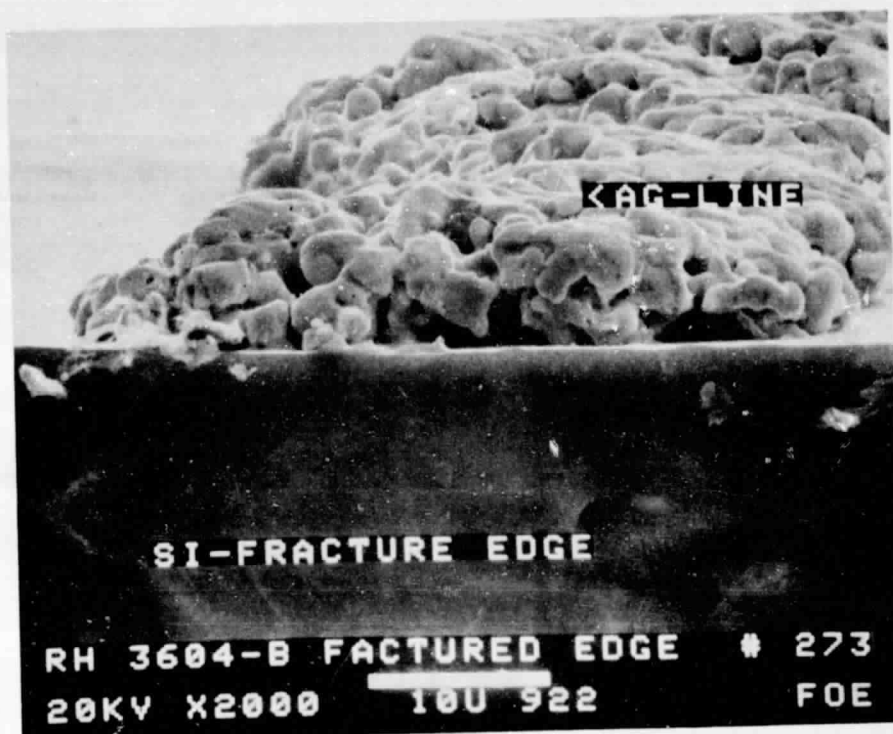Composition 2, 2000X Magnification

Figure 9

Composition 3, 2000X magnification

Figure 10

CROSS SECTION OF GRIDLINE AND SUBSTRATE

Composition 2, 2000X Magnification

Figure 11
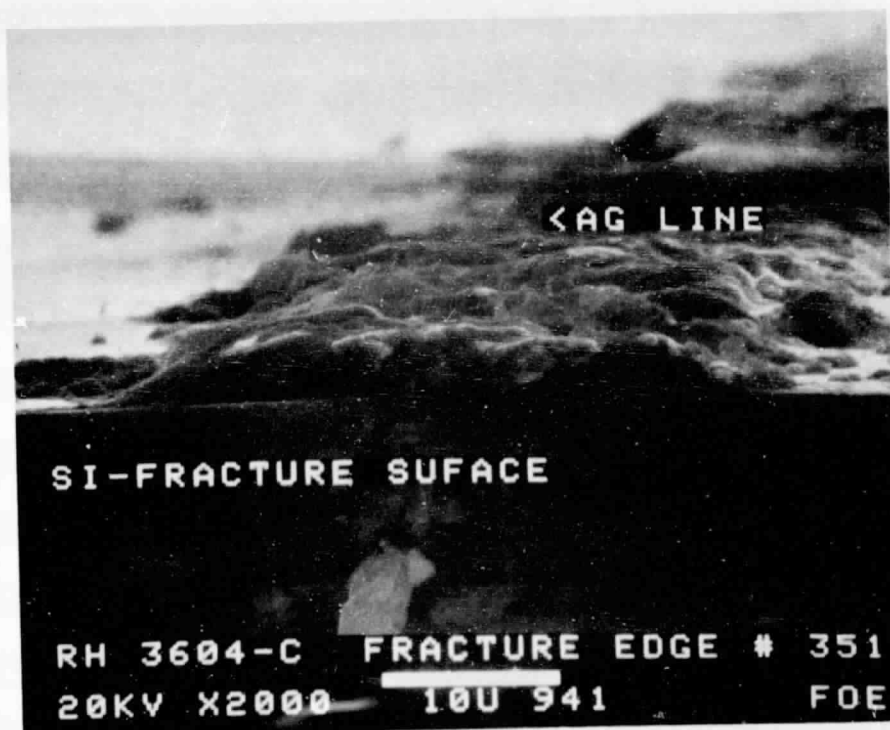
Composition 3, 2000X Magnification

FIGURE 12

Cell Area = 8.41 cm^2

R_{shunt} = 20.0 ohms

η = 9.9%
(No AR Coating)

CURRENT (MA. X 1)

250

200

150

100

50

0

SOLAR CONVERTER E I CURVE

SPECTROLAB   Q C FORM 3001
SYLMAR. CALIFORNIA   DATE: 8-2-79
PROJECT: MIDFILM
SERIAL NO. Lot 2-227
X CELL ☐ MODULE ☐ PANEL DESIGNATION:
227 60 sec. @ 650°C
SOURCE: ☐ SUN X TUNGSTEN ☐ XENON
☐ COLLIMATED   X UNCOLLIMATED
TEST TEMP.: 28 °C _____ °F
TEST NO. 198 in A PROC. NO. 604 mV
Isc = _____   Voc = _____
PMP = _____   BY _____

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7

VOLTAGE (VOLTS X 1.0)

-19-
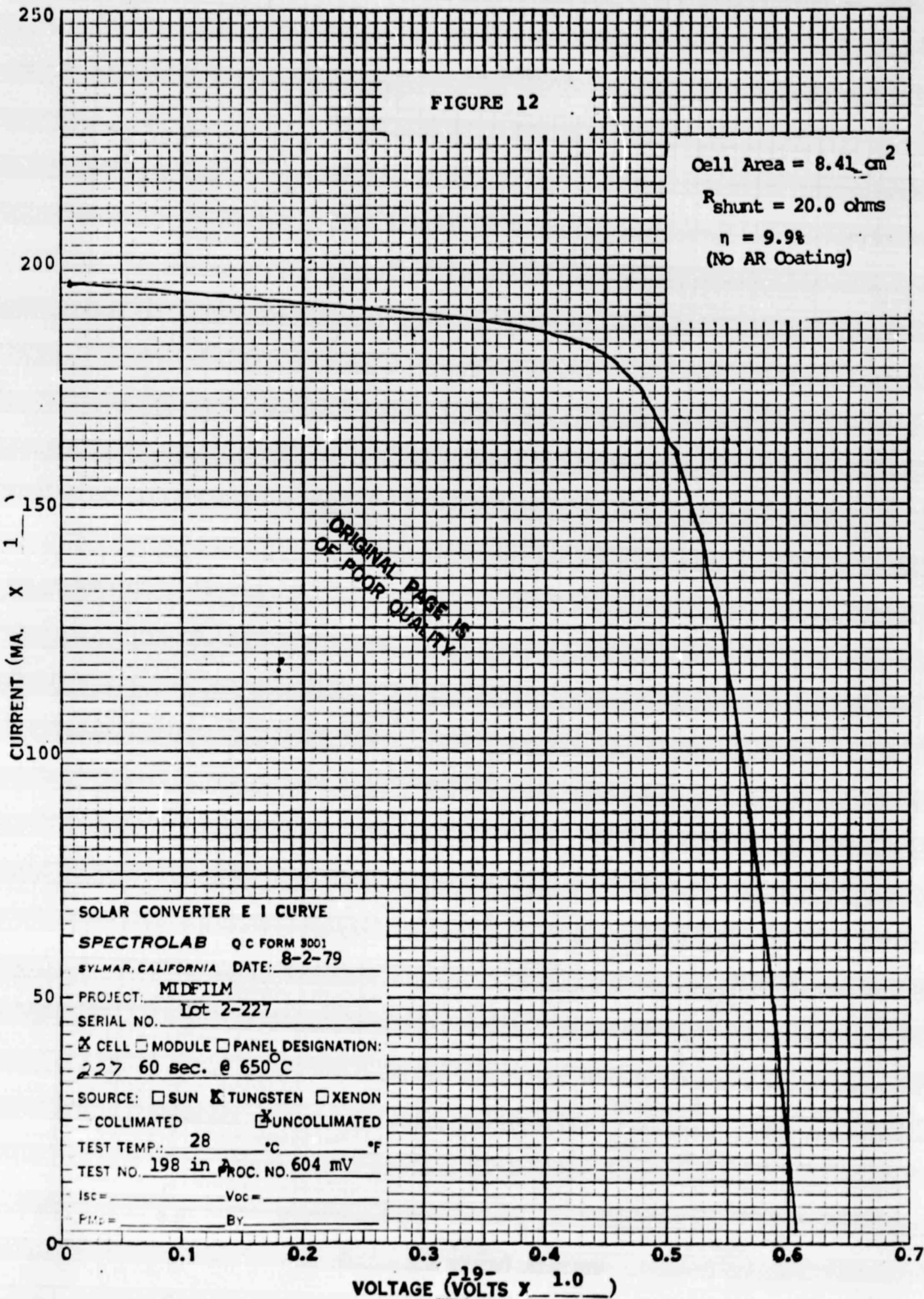
FIGURE 13

Cell Area = 8.41 cm^2

R_{shunt} = 132 ohms

η = 10.5%
(No AR Coating)

SOLAR CONVERTER E I CURVE

SPECTROLAB   Q C FORM 3001

SYLMAR, CALIFORNIA   DATE: 8-2-79

PROJECT: MIDFILM

SERIAL NO. Lot 3-319

☒ CELL ☐ MODULE ☐ PANEL DESIGNATION:
3/9 100 sec. @ 650°C

SOURCE: ☐ SUN ☒ TUNGSTEN ☐ XENON

☐ COLLIMATED   ☒ UNCOLLIMATED

TEST TEMP.: 28 °C _____ °F

TEST NO. 206 PROC. NO. 604 mV

Isc= _____ Voc= _____

PMp= _____ BY _____

3.2   ENVIRONMENTAL EVALUATION
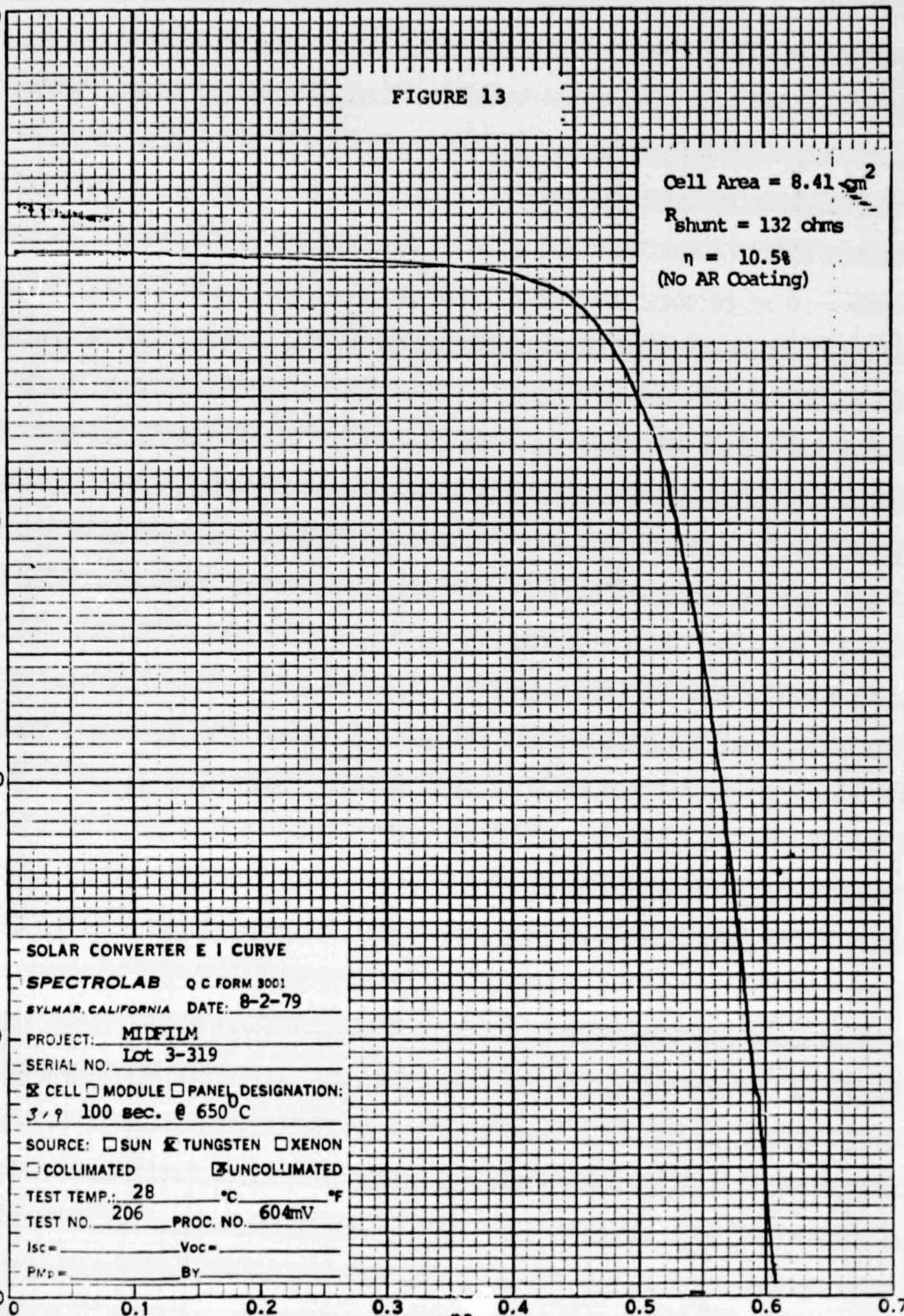
In view of the results of the Exploratory Development Task, com-
position 2 was choosen as a candidate for the environmental
evaluation. A new sixth composition containing 95% Ferro silver
powder and 5% 3347 TFS frit was selected as the second candidate.
This second composition was choosen on the merits of the good
results of the 3347 TFS frit in composition 3 and the good grid-
line continuity and thickness of the "spherical" silver powder
in composition 2.

Three environmental tests selected were conducted:

1)   168 hours at 100% relative humidity and $65^{\circ}C$, followed by
      visual inspection, electrical evaluation and testing for
      adhesion.

2)   Thermal cycle of 50 cycles between + $100^{\circ}C$ and - $40^{\circ}C$ at a
      rate of $3.5^{\circ}/min.$, followed by visual inspection, electrical
      evaluation and testing for adhesion.

3)   Five minutes in boiling deionized water, followed by visual
      inspection, electrical evaluation and testing for adhesion.

A soldering evaluation was conducted by the attachment of a wire
lead to the ohmic by solder techniques, observing ease of soldering
followed by visual examination of solder wetting and measurement
of pull strength.

Ten partially processed wafers were screen printed and fired as
a control sample, Table 8. Cells were fabricated on similar wafers
with silver composition 2 and 6 applied at Ferro Corp. and returned
to Spectrolab after contacts were applied for final silver firing.
The cells from composition 2 had good silver coverage of the grid-
lines as received at Spectrolab, but the cells from composition 6

Table 8

SCREEN PRINTED CONTROL CELLS

Cell No.	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (ohm)	R_{series} (m ohm)
4	596	188	174	156	-
37	607	200	185	29.4	200
69	608	209	193	56.8	100
80	610	207	191	116.3	150
97	607	207	185	38.5	-
102	602	188	172	82.0	-
127	607	203	187	55.6	150
153	592	174	151	53.2	-
168	598	186	170	114	-
190	605	194	152	80.7	-
Average	603.2	145.6	176.0	78.25	
$\hat{\sigma}$	5.98	11.5	15.11	39.94	

had narrow and discontinuous gridlines, possibly damaged by handling.
Cells from each composition were fired at 650°C for 60 to 100 sec.,
Table 9. All these cells showed evidence of silver loss during
the firing process. This loss is one possible cause of gaps and
voids previously reported in the Exploratory Development Task.
In an attempt to prevent silver loss during firing, some cells
were dried between 0 and 20 min., at 200°C prior to firing for
60 sec. at 650°C, Table 10. No definite improvement was observed
with the predrying step.

Infrared drying and firing was attempted on composition 2. The
IR furnace consists of four contolled zones of IR lamps and a 9
inch wide stainless steel belt with a variable speed of 10 to
70 inches/ min. The first two zones were designed for drying
paste contacts in a 36 inch combined drying bank, with a tempera-
ture capability of 0 to 400°C. The second two zones were designed
for the firing of aluminum P^+ or silver contacts in a 24 inch com-
bined firing bank, with a capability of 300 to 1100°C.

As an initial experiment, the drying temperature of the IR fur-
nace was held constant and the firing temperature and belt speed
were varied in order to optimize the cell's output. Table 11
lists the results of this experiment and indicates that a 0, 900,
700, 700 setting for zones 1, 2, 3, 4 respectively to be optimum.
A group of 20 additional cells were fired at these optimum condi-
tions (Table 12) and divided into four groups for the evaluation.
This group of 20 cells had a 15% yield of cells above 14% calcu-
lated efficiency, and 65% yield above 10%. The low yield of this
group of cells is attributed to the high series resistance.

The performance of these IR fired cells is greatly influenced by
the condition of the silver powder prior to firing. Voids and
discontinuous gridlines appear to be the major defects. In
contrast to tube fired cells, loss of silver during firing was
not observed. The initial performance of the cells used in the
environmental evaluation varys in accordance with the degree of
defects present.

-23-

Table 9

650°C TUBE FIRED CELLS

Composition 2

Firing Time	Cell No.	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (ohm)
60 sec.	7	598	201	105	119
	19	597	204	138	92.6
	21	605	203	163	39.1
	98	603	206	105	89.3
	111	594	188	84	90.7
	117	598	193	85	94.3
	125	599	191	118	125.0
	131	604	198	140	66.7
80 sec.	39	598	202	112	73.5
	46	601	198	109	51.6
	51	605	207	145	64.9
	58	607	198	158	131.6
	64	603	208	111	68.2
	133	598	190	69	106
100 sec.	10	591	191	89	83.3
	25	597	200	81	111
	30	595	187	77	96.2
	33	594	199	100	114
	43	591	185	83	43.9

Composition 6

Firing Time	Cell No.	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (ohm)
60 sec.	164	592	199	142	78.1
	181	593	195	139	167
80 sec.	157	593	188	155	73.5
	171	587	164	62	69.4
	172	593	187	89	75.8
	187	592	192	138	78.1

Table 10

DRIED & TUBE FIRED CELLS
60 Sec. at 650°C

Composition	Cell No.	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (ohm)
2	6	600	204	122	69.4
	41	600	202	120	69.4
	93	605	210	119	71.4
	124	597	199	109	53.2
2	Dried 20 minutes @ 200°C				
	60	603	209	131	147
	105	592	186	122	100
	137	604	200	161	36.5
2	Dried 10 minutes @ 200°C				
	16	586	186	73	60.2
	50	606	206	172	56.2
	80 sec. @ 650°C				
6	Dried 20 minutes @ 200°C				
	162	592	193	103	54.4
6	Dried 10 minutes @ 200°C				
	173	579	184	73	27.2
	189	592	173	63	46.3

Table 11

IR FIRED OPTIMIZATION CELLS

Composition 2

Belt Speed	Z1,	Z2,	Z3,	Z4	Cell No.	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (ohm)
35	0,	900,	750,	750	55	601	188	135	92.6
50	0,	900,	750,	750	76	605	196	159	43.9
50	0,	900,	750,	750	13	596	187	125	84.8
48	0,	900,	750,	750	123	593	180	147	69.0
48	0,	900,	725,	725	94	607	210	179	70.7
25	0,	900,	700,	700	15	599	185	131	60.2
25	0,	900,	700,	700	81	604	201	135	55.6
32	0,	900,	700,	700	24	599	191	139	71.4
35	0,	900,	700,	700	89	606	208	149	143
48	0,	900,	700,	700	119	588	187	118	56.6
48	0,	900,	700,	700	75	608	208	186	80.7
50	0,	900,	700,	700	47	600	199	98	119
24	0,	900,	675,	675	122	596	185	140	38.2
32	0,	900,	675,	675	77	607	208	158	106
39	0,	900,	675,	675	96	606	192	151	93.8
48	0,	900,	675,	675	116	590	179	82	254
16	0,	900,	650,	650	12	595	189	113	172
24	0,	900,	650,	650	28	593	163	52	385
32	0,	900,	650,	650	21	583	169	44	263

Table 12

IR FIRED CELLS, POWDER COMPOSITION #2
NO AR COATING
BELT SPEED 48 INCHES/MIN., ZONE 1, 2, 3, 4: 0, 900, 700, 700

Cell No.	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{sh} (ohm)	R_{series} (m-ohm)	η** %
* 8	593	189	99	128.2	-	
36	602	200	121	98.0	890	9.55
38	597	194	132	147.0	615	10.4
40	603	195	144	90.9	560	11.4
42	600	205	124	90.5	825	9.8
*44	597	190	78	167.0	-	
*45	601	199	104	135.0	-	
48	605	199	165	116.0	360	13.0
52	609	205	175	87.7	150	13.8
53	608	202	182	102.0	150	14.4
54	604	199	165	119.0	350	13.0
59	608	203	184	89.3	150	14.5
61	607	202	180	90.9	160	14.2
63	602	196	120	156.0	825	9.5
*65	Broken					
66	605	202	165	116.0	375	13.3
67	608	204	176	200.0	300	13.9
70	605	200	158	109.0	415	12.5
72	597	202	150	128.0	400	11.8
89	603	202	135	104.0	700	10.7
Average	604	201	153	116.0	452	12.2

*Not taken into average.

**I_{500} increased by 34% to account for AR coating.

Environmental evaluations were performed on the composition 2 cells fired in the IR furnace. Table 13 gives a tabulated result of the humidity test. The cell characteristics were measured before and after the 168 hours of 100% humidity at $65^{\circ}C$ and also after a type 600 Scotch tape test. The open circuit voltage (V_{oc}) and series resistance were slightly degraded as a result of this environment. The cells which had good characteristics were practically un-effected by the humid environment, whereas the poor cells had a high degree of degradation. Table 14, gives a tabulation of the thermal cycle test. The cell characteristic did not change during the testing indicating the silver contact is insensitive to the -40 to $100^{\circ}C$ thermal cycle.

Table 15 gives a tabulated result of the boiling water test. The V_{oc} degraded slightly but may be within experimental error. The series resistance was not significantly affected.

Table 16 gives the result of the solder pull test for cell fabricated with powder composition 2 and control screen printed cells. Solder plated copper mesh was reflow soldered on the ohmic collector of the cells with an automatic solder press set at $375^{\circ}C$ for 4 seconds. The solder flowed well and appeared to make a good joint, but the solder leached the silver from the metallization weakening the silver-silicon interface, which was the site of the failures. To prevent solder from leaching the silver metallization, the cell can be held at a elevated temperature ($125^{\circ}C$) and soldered with a tin-lead-silver plated copper ribbon. This procedure reduces the metallization leaching by reducing soldering time and enhances the wettability of the solder onto the silver metallization.

The results of the Environmental Evaluation Task reveal a problem of initially applying the silver powder. The metal must be applied to produce a continuous coverage along the gridlines. Problems may also be occurring in the transporation and storage of the unfired MIDFILM contact. These problems can be eliminated or

Table 13

ENVIRONMENTAL EVALUATION – HUMIDITY TEST

Cell No.	Before Humidity Test					After Humidity Test					After Tape Pull		
	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{shunt} (ohm)	R_{series} (m-ohm)	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{shunt} (ohm)	R_{series} (m-ohm)	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)
59	608	203	184	89	150	606	204	181	106	250	603	204	180
52	609	205	175	88	150	607	208	177	132	350	603	208	166
66	605	202	165	116	375	603	205	154	192	500	601	207	147
40	603	195	144	91	560	598	196	97	132	1150	594	178	79
42	600	205	124	91	825	597	202	99	125	1100	broken		

Table 14

ENVIRONMENTAL EVALUATION – THERMAL CYCLE

Cell No.	Before Thermal Cycle					After Thermal Cycle					After Tape Pull		
	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{shunt} (ohm)	R_{series} (m-ohm)	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{shunt} (ohm)	R_{series} (m-ohm)	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)
61	607	202	180	91	160	605	200	178	91	150	603	198	175
67	608	204	176	200	300	607	201	176	250	250	606	201	175
54	604	199	165	119	350	605	197	162	139	350	603	196	157
72	597	202	150	128	400	599	198	148	135	400	596	201	140
38	597	194	132	147	615	597	188	126	152	700	594	193	126

Table 15

ENVIRONMENTAL EVALUATION - 5 MIN. BOILING

Cell No.	Before Boiling					After Boiling					After Tape Pull		
	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{shunt} (ohm)	R_{series} (m-ohm)	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)	R_{shunt} (ohm)	R_{series} (m-ohm)	V_{oc} (mV)	I_{sc} (mA)	I_{500} (mA)
53	608	202	182	102	150	604	202	172	104	156	604	199	178
70	605	200	158	109	415	602	197	150	109	450	600	196	143
48	605	199	165	116	360	600	197	153	125	365	601	198	155
89	603	202	135	104	700	600	200	130	114	610	599	201	120
36	602	200	121	98	890	598	198	117	100	865	597	198	103

Table 16

PULL TEST

Powder Composition #2, IR Fired Cells

Cell No.	Grams
98	75
122	75
116	100
123	75
63	–
45	100
8	–
119	200
77	200

Screen Printed Cells, Tube Fired

Cell No.	Grams
360	425
341	410
349	500
318	410
376	275
205	500
204	210
301	205
356	500

identified by applying the MIDFILM contact at Spectrolab. If silver powder application appears to be a problem, proper silver powder blends should reduce or eliminate discontinuous gridlines.

3.3   ALTERNATE MATERIALS

The basic concept of the MIDFILM contact is to lower metallization cost. The logical step which follows cell processing achievement seen in the first two tasks of the contact, is to attempt producing the contacts with a low-cost non-silver powder. Three alternate materials, listed in Table 17, were selected for investigation.

Ferro Corp. prepared these powders at their facilities in Ohio. Each powder was used to print the collector grid pattern on silicon discs. An excellent, dense deposit was obtained with all powders. The discs were fired at 700°C for about five minutes (belt speed of 3 inches/minute in a continuous furnace with a 15 inch zone at peak temperature) in an atmosphere of nitrogen containing about 115 parts per million oxygen. The MIDFILM resin was burned off. The copper powder (RH-3622-A) yielded a dense, bright, hard metallization which had a resistivity of 4-5 ohms across the ohmic bar, and approximately 300 ohms for each of the fine gridlines. The nickel (RH-3622-B) and molybdenum (RH-3622-C) oxidized during the fireing and were soft, porous and non-adherent. Nickel was pale green-gray in color, and it appeared that the powder had burst during firing leaving powder scattered over the background areas. The molybdenum was dark brown, but the deposit was undisturbed. However, there was a haze localized around the elements of the pattern separated a very small distance from the deposited powder.

Table 17

COMPOSITIONS FOR ALTERNATE METALS TASK

	RH-3622-A	RH-3622-B	RH-3622-C
Copper Powder (Alpha 00094)	90.25	-	-
Nickel Powder (Inco Type 123)	-	90.25	-
Molybdenum Powder (Atlantic Equipment Engineers Mo 209)	-	-	90.25
Tin Powder (Atlantic Equipment Engineers)	4.75	4.75	4.75
TFS Frit	5.00	5.00	5.00
	100.00	100.00	100.00

In a second experiment, powders RH-3622-A, B and C were fired at 850°C for approximately five minutes in an attempt to develop sintering, particularly in the Ni-Sn and Mo-Sn compositions. A test pattern having a serpentine line 20 mils wide was printed on non-diffused silicon discs. These were fired in atmosphere of nitrogen containing 50 parts per million (PPM) oxygen. The degree of sintering did not appear to be improved, however, some oxidation was evident in all compositions. The nickel and molybdenum compositions were powdery and only a track remained on the substrate after pulling with Scotch tape or light rubbing. The copper composition was best with respect to sintering, having less oxidation and fair adherence. In all samples the tin appeared as spots evenly distributed throughout the metallization.

Previous work with copper indicated that very soft frits, very high in lead oxide content, offered some protection against oxidation. The TFS frit in compositions RH-3622-A and B was replaced with Drakenfeld 2141 W.G. frit and a finer sized copper was used. The composition of these powders, RH-3631-A and B, are given in Table 18. The 640 □ test pattern was printed on silicon discs which were fired five minutes at 700°C in a nitrogen atmosphere with 100 PPM oxygen. Samples printed with RH-3622-A and B were included for comparison. The RH-3631-A sample was better than RH-3622-A in all respects, but still high in resistance (about 70 milliohms/□ in this configuration compared with an open for RH-3622-A). The frit replacement did not show improvement in the nickel compositions.

Additional investigation into the resin burn off indicated that it could be removed in a relatively short firing time at 700°C in an atmosphere of nitrogen containing about 50 parts per million (PPM) oxygen. New tests were conducted with a firing time of 2.5 minutes. Under these conditions, only trace amounts of metal oxidation were detected by x-ray diffraction, with somewhat higher amount being detected in firings of 3.75 minutes duration of peak temperature.

Table 18

COMPOSITIONS FOR ALTERNATE METALS TASK

	RH-3631-A	RH-3631-B	RH-3631-C
Copper Powder (Alpha 00094)	90.25	-	-
Nickel Powder (Inco Type 12)	-	90.25	-
Molybdenum Powder (Atlantic Equipment Engineers Mo 209)	-	-	90.25
Tin Powder (Atlantic Equipment Engineers)	4.75	4.75	4.75
Drakenfeld Fritz Metz "C" Frit	5.00	5.00	5.00
	100.00	100.00	100.00

Electrical continuity was obtained with all three metals in 20 mils wide lines (640 ☐); Cu-235 ohms, Ni-1.5 megohms, Mo-8 megohms. The results indicate that short duration firing at 700°C can be achieved for base metal metallizations applied by the MIDFILM process. The second finding is that the compositions used do not mature into well sintered, adherent metallizations even when fired for five minutes at 950°C (nitrogen containing 15 PPM oxygen). Some sintering of the nickel and molybdenum powders did take place as evidenced by resistance readings on 20 mil wide lines (640 ☐) on alumina of 175 ohms for nickel and 865 ohms for molybdenum (copper was not fired). However, the deposits were powdery and easily removed by rubbing or with Scotch Tape. Metal powders with better sintering properties than the grades used in these tests would have to be sought for further work in these systems.

Each of the compositions RH-3634-A, RH-3634-B, and RH-3634-C, Table 17 was used to deposit the grid pattern on ten (10) silicon wafers. Eight with composition RH-3634-A and nine (9) each with compositions RH-3634-B and RH-3634-C were sent to Spectrolab for firing. The remaining samples were fired at Ferro (700°C, 2.5 minutes, nitrogen with 50 PPM oxygen) and were shipped to Spectrolab for final processing.

The I-V cell characteristics were measured at Spectrolab on wafers metallized and fired at Ferro (Figure 14). The cell processed with the copper-tin (RH-3634-A) composition had a good physical appearance but the I-V curve indicates junction degradation. The cells processed with the nickel-tin (RH-3622-B) and molybdenum-tin (RH-3622-C) appear heavily oxidized and the I-V curve indicates high series resistance.

Wafers from each composition were fired in a IR furnace at Spectrolab which totally oxidized the contacts. The copper-tin composition was also fired in a tube furnace with a high flow of nitrogen for 30 seconds at 700°C. This experiment also resulted in oxidized contacts. These contacts are very sensitive to the oxidizing

Figure 1.

CURRENT (MA. X 4.0)

100
90
80
70
60
50
40
30
20
10
0

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7

VOLTAGE (VOLTS X 1.0)

Mo-Sn metallization

Ni-Sn metallization

Cu-Sn metallization

SOLAR CONVERTER E I CURVE

SPECTROLAB   Q C FORM 3001

SYLMAR. CALIFORNIA   DATE: 12/10/80

PROJECT: MIDFILM

SERIAL NO. Alternate Mat.

X CELL □ MODULE □ PANEL DESIGNATION: FM1

SOURCE: □ SUN X TUNGSTEN □ XENON

□ COLLIMATED   X UNCOLLIMATED

TEST TEMP.: 28   °C   °F

TEST NO   PROC. NO.

Isc =   Voc =

Pmp =   BY

potential of the firing atmosphere. The conflicting requirement for oxidation to ash the photoresist will place strongest requirements on control of the firing atmosphere.

Progress of the alternate materials were very limited but useful information was obtained. The photoresin could be removed with small amounts of oxygen (50 PPM) at 700°C. The copper-tin was the only composition that could be fired in a oxidizing atmosphere without being totally oxidized. The copper-tin composition degraded the cell response. Similiar results of copper degradation has been reported by other contractors. The photoresin could not be removed from the nickel-tin and molybdenum-tin compositions without oxidizing the metals. Alternative cell processing which would remove the photoresin (possible with a plasma) prior to sintering in an inert atmosphere may be possible with these metals.

4.0 CONCLUSIONS

The MIDFILM contact has been demonstrated to produce cells of efficiencies above 14% (AM1, 28°C). Powder compositions similar to those of screen printed silver paste appear acceptable for MIDFILM metallization. Low yield in the MIDFILM metallization has been traced to discontinuous gridlines, resulting in high series resistance. The discontinuity of the gridlines on some wafers was observed prior to firing the contacts. The cells with high series resistance degraded further during the humidity test, whereas the cells with low series resistance were practically uneffected. Current reflow soldering techniques used on screen printed contacts leached the silver from the MIDFILM contact. Alternate solder procedures must be established to prevent leaching.

Investigation of alternative materials (other than silver) reveal problems with ashing the photoresin without oxidizing the metals. The copper-tin-frit composition was the only one that was fired successfully with nitrogen and 50 PPM oxygen and resulted in a degradation of the wafer. Both the nickel-tin-frit and the molybdenum-tin-frit contacts oxidized during the ashing of the photoresin but they did not show the same type of cell degradation observed in the copper system. The degradation seen, appears to be a series resistance problem associated with the oxidation of the contact.

Optimum metallization powder compositions, MIDFILM application parameters and firing conditions were not established. Adequate plated interconnections and soldering techniques were not established. Additional development effort is needed in order to resolve these matters and to consistently attain high efficiency and yield.

APPENDIX 1

CLEANING PROCEDURE*

(PRIOR TO APPLICATION OF PHOTO RESIST.)

1. 10 vol. % HCl dip for 60 sec. (RT)

2. 10 vol. % HF dip for 60 sec. and rinse in DI water (RT)

3. 50 vol. % acetic acid dip for 60 sec.

4. 30 seconds rinse in hot D.I. water (70-95°C)

5. Rinse in beaker of acetone (RT)

6. Rinse in another beaker of acetone 2 min. (RT)

7. Rinse in alcohol 2 min. (RT)

8. Two min. rinse in hot D.I. water (70-95°C)

9. Rinse in D.I. water and dry (RT)

10. Rinse in alcohol and dry (RT)

* This cleaning procedure was shown under another JPL contract, to remove any residual contaminates and prepare the surface for metallization. No effort was undertaken in this contact to reduce the number of sets in the process.

APPENDIX 2

DEPOSITION OF SILVER POWDER ON SILICON SUBSTRATE
by MIDFILM ® PROCESS

1. MIDFILM resin, RC4851, was applied by spinning for 40
   seconds at 2200 RPM. The edges and back of the wafer
   were wiped with solvent to remove resin. A dry resin
   weight of four (4) milligrams per square inch was
   sought and the application weight was determined at
   a frequency of about 1 in 8 wafers. Before applying
   the resin the substrates were spin-rinsed with 1,1,1
   trichloroethane.

2. The coated substrates were exposed to ultraviolet light
   (16-17 mW/cm^2 -3650 A.V.), through the appropriate mask,
   for eight (8) seconds.

3. Silver powder was deposited on the exposed surface from
   a spatula and lightly rubbed in a rotary motion with
   a soft, deep-piled pad to develop the pattern and to
   remove powder from the background area.

3. Each finished sample was exposed to the U.V. light for
   eight seconds to harden the metallization--done only for
   withstanding better the rigors of transporting in the
   unfired condition.

Appendix 3

CALCULATION OF SERIES RESISTANCE
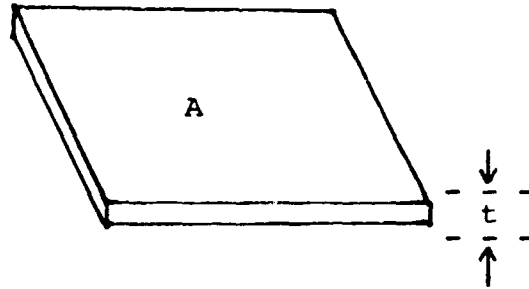
A) BASE MATERIAL RESISTANCE

R = resistance

ρ_{Si} = resistivity of silicon

t = thickness of wafer

A = area of wafer
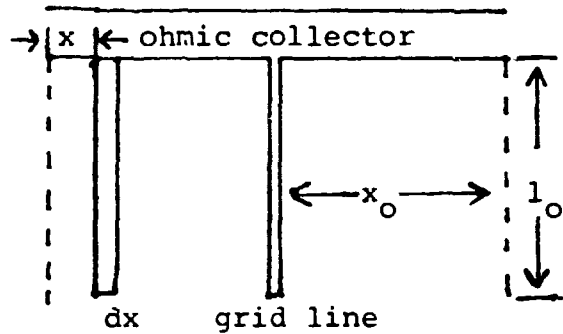
$$R = \frac{\rho_{Si}\, t}{A} \qquad (1)$$

B) RESISTANCE OF DIFFUSED SURFACE LAYER

ρ_s = surface resistivity

l_o = length of grid line
(assuming grid lines go to edge of wafer)

x_o = half distance between grid lines

j = current density*

The element of power loss over an element of silicon dx, is the square of the current entering that element times the resistance of that element dx.

$$dp = (j l_o x)^2 \cdot \left(\rho_s \frac{dx}{l_o} \right) \qquad (2)$$

$$dp = j l_o \rho_s\, x^2 dx \qquad (3)$$

integrating over the half distance between grid lines (x_o) gives the total voltage drop to the midpoint.

*As a first approximation of power loss, the current density (j) is assumed to be independent of distance from gridline.

$$\Delta p = j^2 \rho_s l_o \int_0^{x_o} x^2 dx$$

$$= 1/3 \ j^2 \rho_s l_o \ x^3 \Big|_0^{x_o}$$

$$\Delta p = 1/3 \ j^2 \rho_s l_o \ x_o^3 \qquad (4)$$

The total resistance over the half distance between grid lines is;

$$R = \frac{\Delta p}{j^2 l_o^2 \ x_o^2} \qquad (5)$$

$$= \frac{\rho_s \ x_o}{3 l_o} \qquad (6)$$

These areas of half distance between grid lines are all in parallel.

$$R_{total} = \frac{\rho_s \ x_o}{3 l_o} \ \div \ \text{number of areas} \qquad (7)$$

C) RESISTANCE OF GRID LINES

ρ_{Ag} = resistivity of silver paste

l_o = length of grid lines (assuming grid lines go to edge of wafer)

W = width of grid line

H = height of grid line

x_o = half distance between grid lines

j = current density
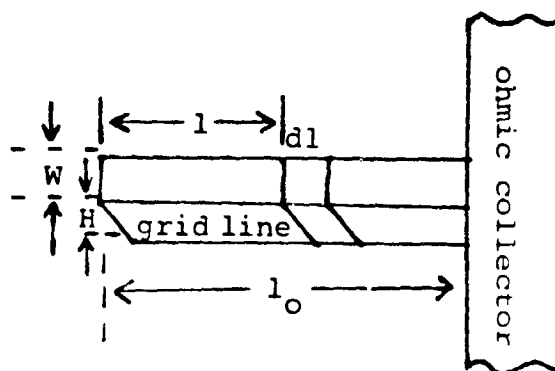
The element of power loss over an element of grid line dl, is the square of the current entering that element times the resistance of that element dl.

$$dp = (2 \, x_o \, j \, l)^2 \cdot \left(\frac{\rho_{Ag} \, dl}{WH} \right) \quad (8)$$

$$dp = \frac{4j^2 \, \rho_{Ag} \, x_o^2 \, l^2 dl}{WH} \quad (9)$$

integrating over the grid line gives the total power loss for the grid line.

$$\Delta P = \frac{4j^2 \rho_{Ag} \, x_o^2}{WH} \int_o^{l_o} l^2 dl$$

$$\Delta P = \frac{4j^2 \, \rho_{Ag} \, x_o^2 \, l_o^3}{3 \quad WH} \quad (10)$$

The total resistance over the grid lines is:

$$R = \frac{\Delta P}{4 \, x_o^2 \, j^2 \, l_o^2}$$

$$= \frac{\rho_{Ag} \, l_o}{3 \, WH} \quad (11)$$

The grid lines are in parallel, therefore

$$R_{total} = \frac{\rho_{Ag} \, l_o}{3 \, WH} \div \text{number of grid lines} \quad (12)$$

D) OHMIC COLLECTOR

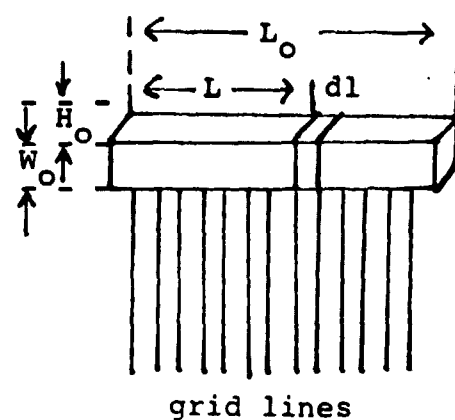ρ_{Ag} = resistivity of **silver paste**

l_o = length of grid lines

W_o = width of ohmic collector

H_o = height of ohmic collector

L_o = length of ohmic collector

j = current density

grid lines

a expression similar to that of equation 11 can
be derived:

$$R = \frac{\rho_{Ag} \, L_o}{3 \, W_o H_o}$$

(13)

Depending on the number of pick ups and distance between them the
total resistance of the ohmic collector will be reduced.

SAMPLE CALCULATION OF SERIES RESISTANCE

FOR COMPOSITION 2

ρ_{si} = 1.0 Ω-cm

t = 0.033 cm

A = 8.41 cm^2

ρ_s = 35 Ω/

l_o = 1.89 cm

X_o = 0.0404 cm

ρ_{Ag} = 4.77 x 10^{-6} Ω-cm

W = 4.6 x 10^{-3} cm

H = 0.85 x 10^{-3} cm

W_o = 78.8 x 10^{-3} cm

H_o = 0.85 x 10^{-3} cm

L_o = 4.023 cm

Number of gridlines = 48

A) Base Material Resistance

$$R = \frac{\rho_{si}\ t}{A} = \frac{(1.0)(0.033)}{8.41}\ \Omega = 3.92\ m\Omega$$

B) Resistance of Diffused Surface Layer

$$R = \frac{\rho_s\ X_o}{3\ l_o}\ \div\ 96 = \frac{(35)(0.0404)}{3(1.89)}\ \Omega\ \div\ 96 = 2.53\ m\Omega$$

C) Resistance of Gridlines

$$R = \frac{\rho_{Ag}\ l_o}{3\ WH}\ \div\ 48 = \frac{(4.77\ x\ 10^{-6})(1.89)\ \Omega}{3(4.6\ x\ 10^{-3})(0.85\ x\ 10^{-3})}\ \div\ 48 = 16\ m\Omega$$

D) Resitance of ohmic collector

$$R = \frac{\rho_{Ag}\ L_o}{3\ W_o H_o} = \frac{(4.77\ x\ 10^{-6})(4.023)}{3(78.8\ x\ 10^{-3})(0.85\ x10^{-3})}\ \Omega = 95.5\ m\Omega$$

The test fixture contacts ohmic collector in two locations 0.5
cm off center. This test fixture reduces series resistance by
a factor of 0.047. Therefore:

$$R = 95.5 \times 0.047 = 4.49 \text{ m}\Omega$$

Total resistance of contact pattern is:

$$3.92 + 2.53 + 16.0 + 4.49 = 28.33 \text{ m}\Omega$$